

FLUORINE COMPOUNDS, INORGANIC, MOLYBDENUM

1. Molybdenum Hexafluoride

Molybdenum hexafluoride [7783-77-9], MoF_6 , is a volatile liquid at room temperature. It is very moisture sensitive, hydrolyzing immediately upon contact with water to produce HF and molybdenum oxyfluorides. MoF_6 should therefore be handled in a closed system or in a vacuum line located in a chemical hood. The crystals possess a body-centered cubic structure that changes to orthorhombic below -96°C (1, 2). The known physical properties are listed in Table 1.

Molybdenum hexafluoride can be prepared by the action of elemental fluorine on hydrogen-reduced molybdenum powder (100–300 mesh (ca 149–46 μm)) at 200°C . The reaction starts at 150°C . Owing to the heat of reaction, the temperature of the reactor rises quickly but it can be controlled by increasing the flow rate of the carrier gas, argon, or reducing the flow of fluorine.

Molybdenum hexafluoride is used in the manufacture of thin films (qv) for large-scale integrated circuits (qv) commonly known as LSIC systems (3, 4), in the manufacture of metallized ceramics (see Metal-matrix composites) (5), and chemical vapor deposition of molybdenum and molybdenum–tungsten alloys (see Molybdenum and molybdenum alloys) (6, 7). The latter process involves the reduction of gaseous metal fluorides by hydrogen at elevated temperatures to produce metals or their alloys such as molybdenum–tungsten, molybdenum–tungsten–rhenium, or molybdenum–rhenium alloys.

Molybdenum hexafluoride is classified as a corrosive and poison gas. It is stored and shipped in steel, stainless steel, or Monel cylinders approved by DOT. Electronic and semiconductor industries prefer the cylinders equipped with valves which have Compressed Gas Association (CGA) 330 outlets. This material is produced on pilot-plant scale and the U.S. annual consumption is less than 50 kg/yr. As of 1993, the price was \$1500/kg. It is available from Advance Research Chemicals Inc., Aldrich Chemicals, Atomergic, Cerac, Johnson/Matthey, Pfaltz & Bauer, and Strem Chemicals.

2. Other Molybdenum Fluorides

Three other binary compounds of molybdenum and fluorine are known to exist: molybdenum trifluoride [20193-58-2], MoF_3 , molybdenum tetrafluoride [23412-45-5], MoF_4 , and molybdenum pentafluoride [13819-84-6], MoF_5 . Also known are the two oxyfluorides, molybdenum dioxydifluoride [13824-57-2], MoO_2F_2 , and molybdenum oxytetrafluoride [14459-59-7], MoOF_4 . The use of these other compounds is limited to research applications.

2 FLUORINE COMPOUNDS, INORGANIC, MOLYBDENUM

Table 1. Physical Properties of MoF₆

Property	Value
mol wt	209.93
melting point, °C	17.4
boiling point, °C	35.0
solubility, g/100 g	^a
density, g/cm ³	
liquid	2.544
solid	2.888
ΔH_f , kJ/mol ^b	
liquid	−1626
gas	−1558
ΔG_f , kJ/mol ^b	
liquid	−1511
gas	−1468
S, J/(mol·K) ^b	259.69

^a Hydrolyzes in water.

^b To convert J to cal, divide by 4.184.

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